1972
international book year

KFKI-72-5

J. Szőke

ON-LINE MEASUREMENTS AND COMPUTERIZED DATA PROCESSING OF SPECTRA

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

KFKI-72-5

J. SZÖKE

COMPUTERIZED MEASUREMENTS AND DATA PROCESSING

4. ON-LINE MEASUREMENTS AND COMPUTERIZED DATA PROCESSING OF SPECTRA

ABSTRACT

A description is given of a computerized measuring centre for optical spectroscopy, established at the Central Research Institute for Physics, Budapest, with which measured data from a set of instruments covering the entire spectrum can be collected and prepared on-line for evalution on a large computer. The steps employed in spectral data processing and experiences and conclusions gained by the author in applying these techniques are dealt with in some detail.

KIVONAT

A szerző ismerteti a Központi Fizikai Kutató Intézetben létrehozott optikai spektroszkópiai komputeres mérőközpontot, amely a teljes spektrumot átfogó müszerpark digitális mérési adatait on-line módon gyüjti és előkészíti nagy-komputeres adatkiértékelésre.

A közlemény ismerteti a szinképi adatfeldolgozás menetét, a szerző által vizsgált módszerek alkalmazása kapcsán nyert tapasztalatokat és megállapitásokat.

РЕЗЮМЕ

Описывается оптическо-спектроскопический измерительный центр, основывающийся на использовании ЭВМ, созданный в Центральном институте физических исследований. Измерительный центр собирает и подготавливает к обработке на большой ЭВМ цифровые данные, полученные с помощью приборов для измерения спектра. Излагаются ход обработки спектроскопических данных, опыт, приобретенный автором в связи с применением использованных им методов.

INTRODUCTION

Modern research work concerned with materials requires an ever increasing amount of possibly precise information on mulecular structures and physical parameters. Spectroscopic methods are especially valuable in this field, because spectra represent all the interactions between the structural elements of matter and the electromagnetic field. The complete spectroscopic description of any material - as can be seen in Fig. 1 - requires a number

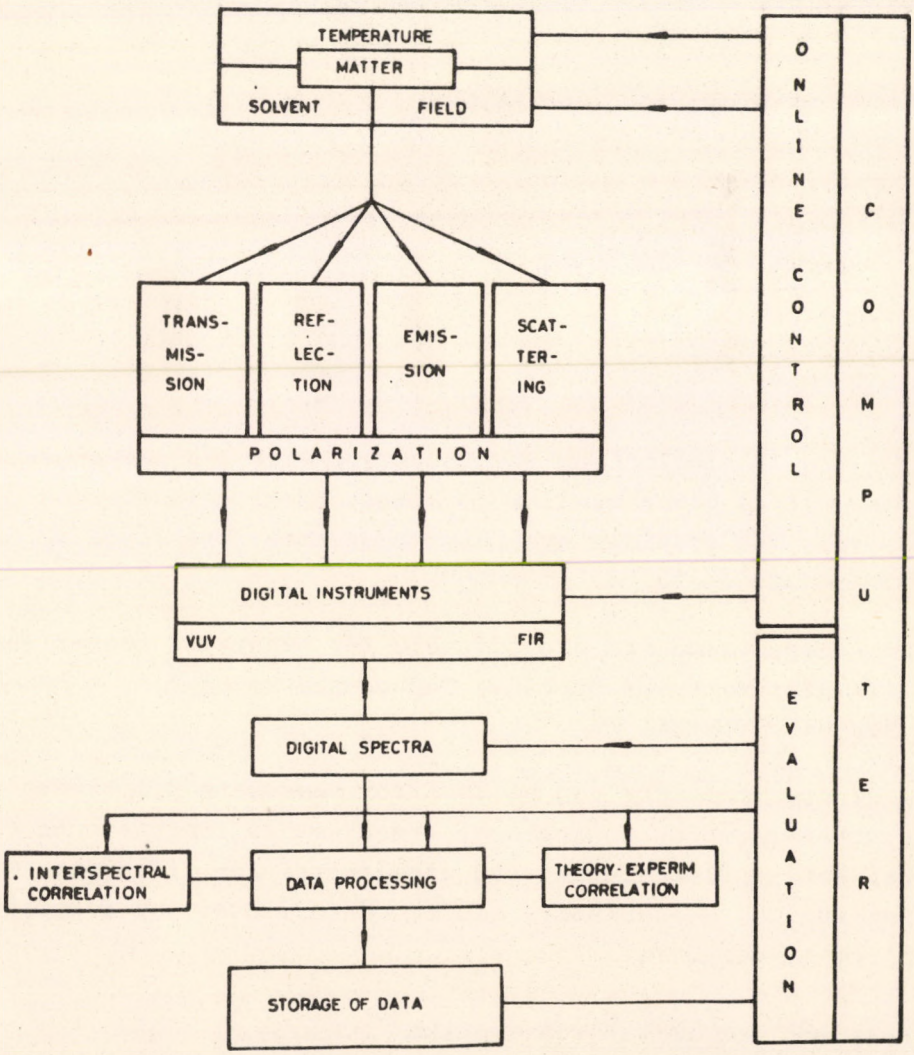


Fig. 1 Scheme of the computerized spectroscopic work

of spectra made under different conditions of electric and magnetic fields, medium, temperature, etc. and with the use of several types of measurement /absorption, reflection, emission and scattering/ covering the whole optical spectrum. In the evaluation work it is necessary to study the correlations between the different experimental spectra and those between the experimental and theoretical spectroscopic results. But the spectra themselves, and the problems of their interpretation are complex in nature, thus their evaluation demands much time and extensive human intervention. The only realistic approach that offers the possibility of the easy typifying of the results and yet remains sufficiently flexible in its operation is the use of computer methods, despite the hard work that must be put into selecting the best procedures and determining the limits of their application. /Fig. 1./

In this paper the results of the systematic work carried out in this field at the Central Research Institute for Physics, Budapest are described.

I. COMPUTERIZED SPECTROSCOPIC LABORATORY

A really effective optical spectroscopic laboratory must have four types of instruments. With reference to the instrument set built at our laboratory, these are as follows:

1/ Vacuum UV spectrometer with concave grating, applicable in the range from 80000 to 40000 cm^{-1}.

2/ Several UV and IR single-beam spectrometers with 1 m plane-grating monochromators as well as other similar constructions with different detectors and grating sets. The gratings are interchangeable. The range of application is from 50000 to 300 cm^{-1}.

The IR spectrometers are suitable for measuring transmission, reflection, and molecular emission spectra. The sample is held in a termaperature-controlled helium cryostat.

The UV spectrometers can be used for measuring all types of electronic transitions: transmission, reflection, steady-state luminescence and excitation spectra, and singlet-singlet and singlet-triplet lifetimes, with or without polarization. Measurements can be performed at any temperature between room and helium temperature.

3/ Interferometers for IR and FIR regions

Michelson-type interferometers. An IR version is under development. The FIR region is used from 600 to 10 cm^{-1}. The sample is held in a helium cryostat.

4/ Scattering photometer for Raman spectroscopy

A photometer of this type is now being developed in our laboratory. Spectrometers of the above types have been in use for a considerable time, but recently we had to modify the conventional instruments for new tasks. The following principles were adopted in our constructions.

All instruments must work	applies to
- fast - at high scanning speed	the schanning mechanism
- periodically - in a single-beam mode operation	the optical units
- automatically - with a high stability in time	the whole instrument

The measurements are performed using a photon counter and/or a lock-in amplifier with four parallel gain outputs in decimal steps /1.10, 100, 1000/. The digital resolution in all outputs is 12 bits.

The analogue or digital results are transferred through a 60 m cable to the computer center /See Fig. 2/ and then are fed, either directly, or

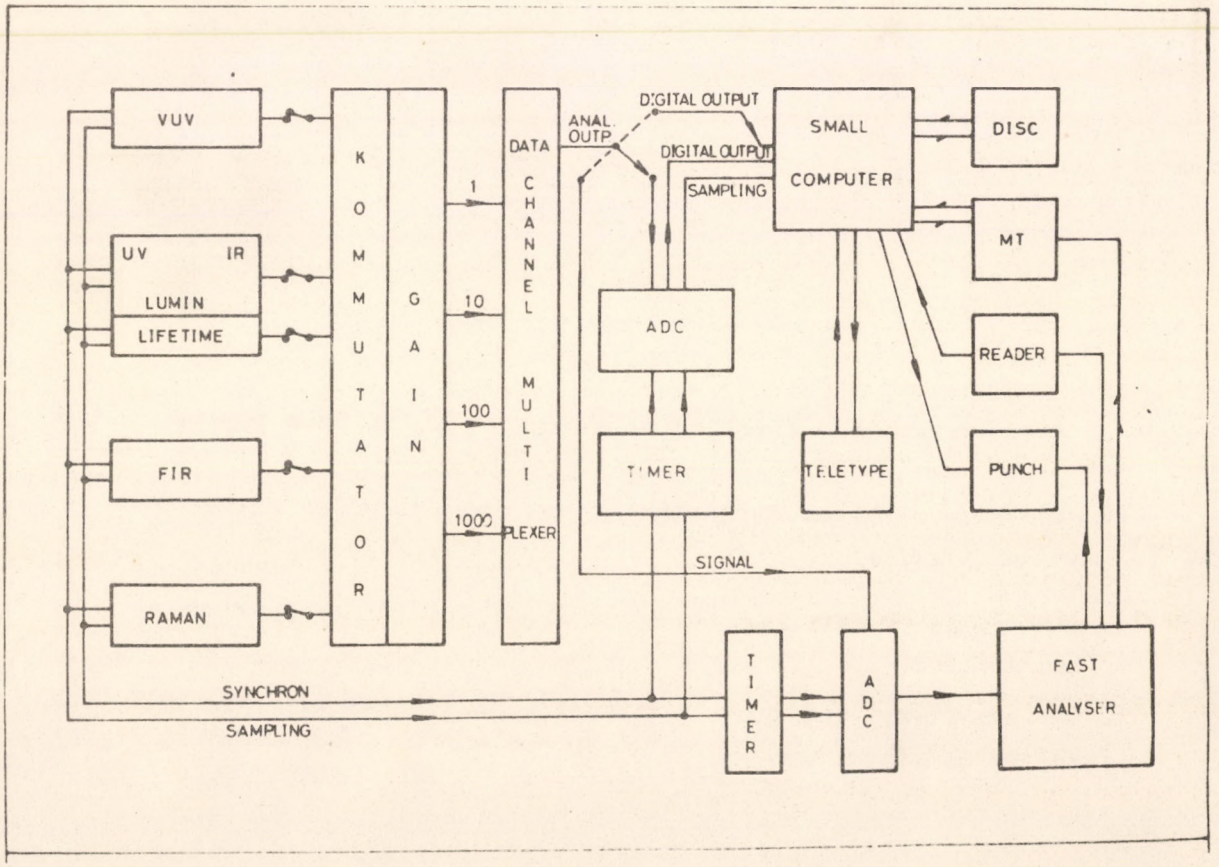


Fig.2 Organization of the on-line computerized spectroscopic laboratory

after analogue-to-digital conversion, through a computer-controlled data channel multiplexer into the computer memory. The start and sampling signals are generated by the spectrometer. The analogue-to-digital conversion and the computer storage are automatized by a timer. After the measuring process the data are recorded on magnetic tape. All computer programs are stored in a disc memory from which the necessary parts can be retrieved.

In the computer center there is a small computer /TPA-1001/ with its different input and output peripherials. An analyser system which can be used with a fast timer and serves as another facility for high-speed measurements is also used in the center. Its maximum sampling speed is 5 μsec. Lifetimes in the nsec range can be measured by a Berlman-type instrument [1] modified for the needs of our measuring system. /Fig. 3/

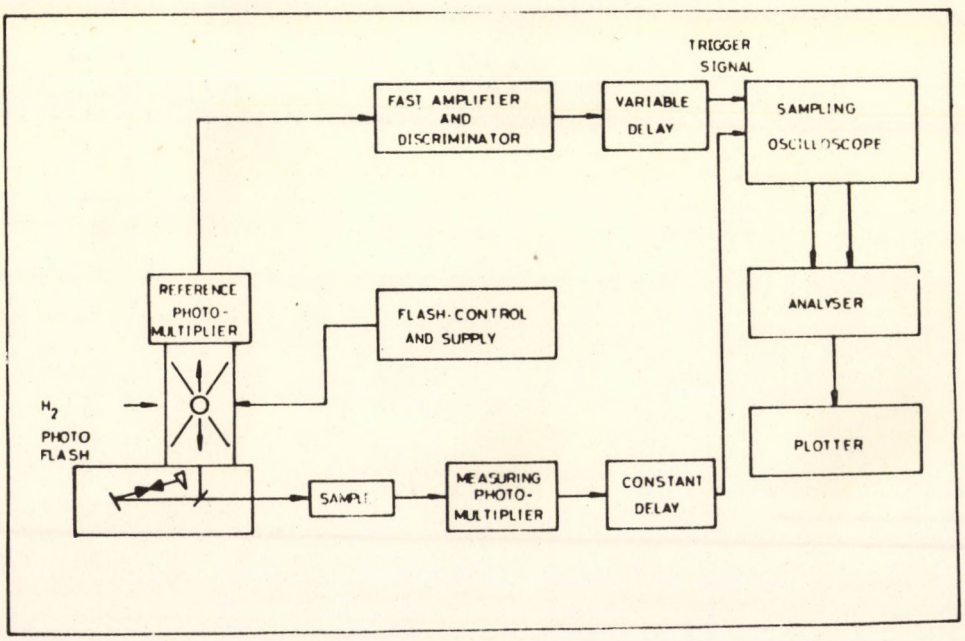


Fig. 3 Arrangement for lifetime measurement in the nsec region

The working cycle of our computerized spectroscopic equipment is the following: /Fig. 4/

a/ The computer gives an analogue signal to the temperature controller.

b/ If necessary, the gain is manually controlled with the aid of an oscilloscope.

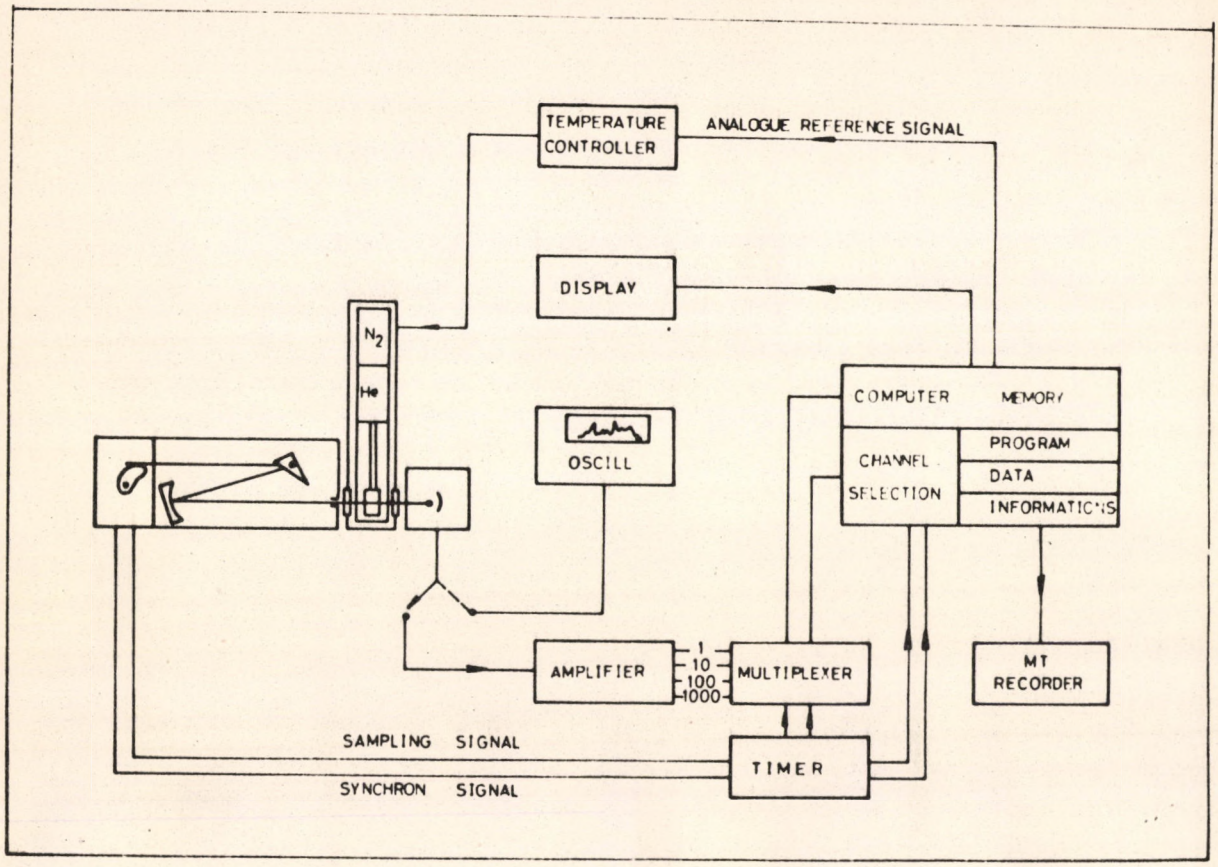


Fig. 4 Outline of the on-line measurement

c/ The amplification is stored in the computer memory.

d/ The maximum signal is set manually.

e/ The data are fed into the memory /maximum 3000 data/. The noise level is determined and the necessary number of measuring cycles is calculated.

f/ The measuring cycle is started manually. The timer transmits the sampling signals only after the synchronizing signal has been received.

g/ The measuring cycle is carried out as follows: In the first cycle, on storing instruction, the computer examines all the channels with maximum information content and feeds this content and the channel number, into the memory. During and after the measuring cycle the stored spectrum can be seen on parallel display in the spectroscopic and computer laboratories.

h/ The second cycle begins on the appearence of a new start pulse. The results are read by the computer point by point from the

channel chosen in the first cycle and a weighted average is calculated from the stored and new values and also stored. When the prescribed number of cycles is exhausted, the measurement is finished and the computer waits for further manual instructions.

j/ If the visually inspected display figure is acceptable, the data are recorded on magnetic tape.

The magnetic tape recorder consists of a commercial tape recorder and an interfaœ from which the data can be passed through a satellite small computer /TPA 1001/ into an ICT-1905 computer.

Before computer evaluation all the stored spectra are plotted by an X,Y-ray recorder directly from the magnetic tape.

II. DATA PROCESSING

The digital spectra are evaluated in a big computer by subroutines developed specially for data processing and are called the standard library routines. The organization is suitable for the compilation of simple MAIN programs.

1/ Correlations and calibrations

In the first step the data of the measured spectra must be corrected and calibrated to eliminate instrumental distortions appearing in the numerical values of x- and y-coordinates.

a/ x-coordinates

The exact values of the x-coordinate for every data can be determined only by a spectral lamp calibration procedure. The calibration curve is calculated by polynomial approximation.

b/ y-coordinates

Distortions caused by the instrument characteristics can be eliminated by using special test material /e.g. quinine sulphate in fluorescence spectroscopy/. In these cases reported data are usually applied. The deviation of our measurements from the reported data gives a correction array. Errors in the reported data do not cause any problem in the evaluation since the digital results can be corrected again at any time.

c/ Adjustment of regions

This is important for electronic absorption spectroscopy where the complete spectrum consists of several fragments. In our experience only the Lambert law is applicable, even though it involves heavy technical problems. The Beer law is valid only for low concentrations.

2/ Transformations

First step in the evaluation work is to transform the data into a suitable form for the estimation. This procedure is extended to both the x- and y-coordinates.

a/ x-coordinates

A number of variables are used to express the energy of the radiation field /erg, cal/mol, ν, ν^*, fresnel, eV etc/ or the length of waves /A, nm, μm, mμ, etc/. The transformation processes are available in the library as standard functions.

b/ y-coordinates

The values of the y-coordiante give the intensity of the light-matter interactions. Basically two types of spectra can be distinguished from this point of view: relative and absolute spectra. In the first case, it is necessary to calculate the ratio of two single-beam spectra. Since the intensity values vary in a wide range, a logarithmic representation is very often used. This form of spectrum is applied for storing, too.

c/ Interferograms

In contrast to conventional spectrometers, interferometers do not contain a dispersive element, so the detector can not discriminate between different radiation frequencies. The interferogram produced by the usually applied Michelson-type interformeters transforms the polychromatic signal as a whole. The intensity data can be described by the simple cosine transform

$$I(x) = \int_{-\infty}^{+\infty} I(\nu) \cos(2\pi \, x \, \nu) d\nu$$

where $I(x)$ is the intensity of the output signal as a function of the mirror displacement x /integrated intensity at path difference x/ and $I(\nu)$ is the intensity value at frequency ν, which can be obtained by the Fourier transform

$$I(\nu) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi.x.\nu)dx$$

This simple procedure, in general, gives a very good spectrum, however, it is difficult to construct interferometers which are perfectly compensated over the wide frequency range, and this limitation leads to the appearance of sine components in the interferogram. The general description of an interferogram is given by the following complex Fourier transform pair:

$$I(x) = \int_{-\infty}^{+\infty} I(\nu) \exp[2\pi.i.x.\nu]\ d\nu$$

and

$$I(\nu) = \int_{-\infty}^{+\infty} I(x) \exp[-2\pi.i.x.\nu]dx$$

Since the interferogram is an experimental result, the second transform has to be calculated. Richards [2] suggests the following cosine algorithm for computer evaluation

$$I(\nu_i) = F_o + 2 \sum_{n=1}^{N} F_n \cos(n.\nu_i.\pi/N)$$

where N is the path difference and N is the number of experimental points in the frequency region studied. A is the average value of the last 10 points and F_o is the intensity at zero path difference while F_n is the experimental intensity value of the interferogram after apodization /in Richard's procedure $F_n = I(x_n - A)$/.

In Fig. 5 the interferogram and the high resolution transform of the spectrum of uranyl-tris-carbonate can be seen.

3/ Smoothing

This procedure is important from the point of view of data-processing, since the mathematical approximations used are very sensitive to the noise superimposed on the information. A number of methods of eliminating noise from spectra are known. The most frequently used of these are:

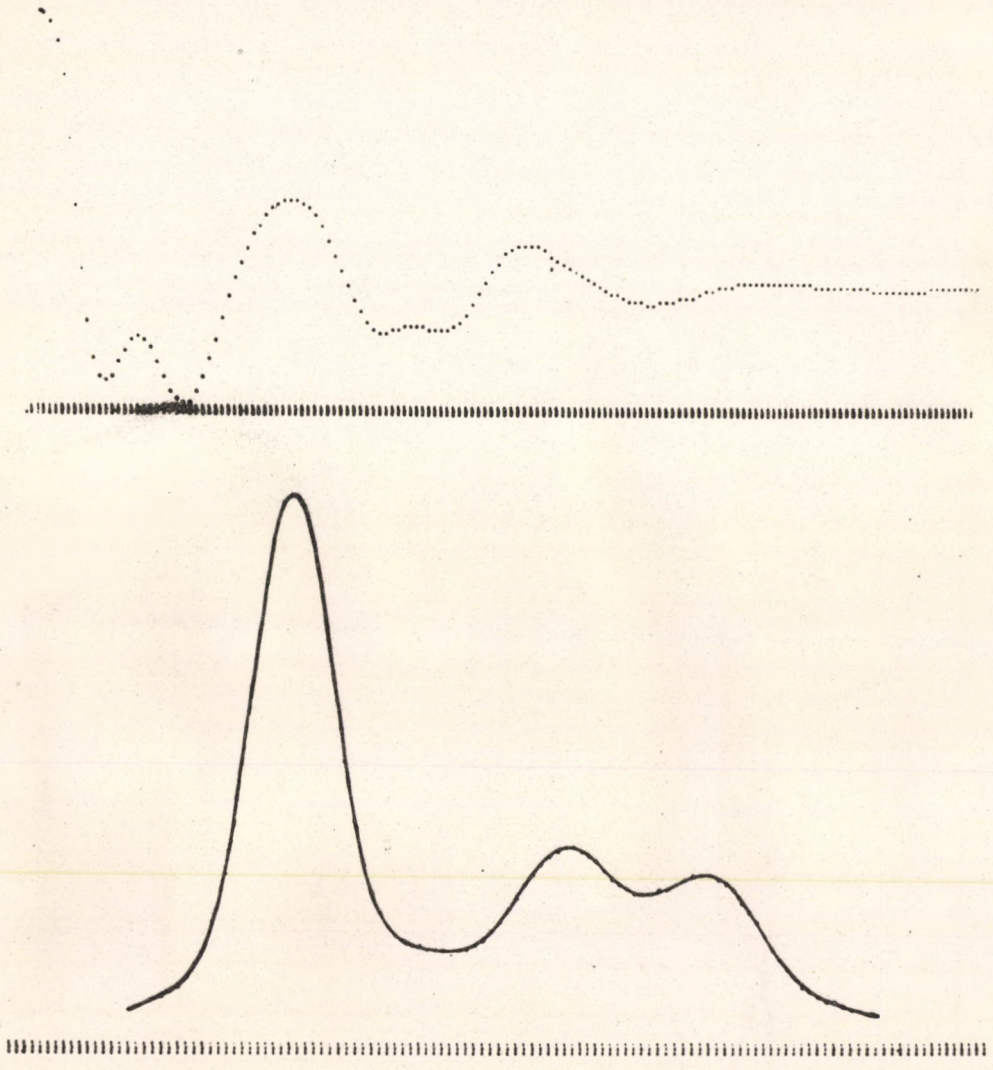
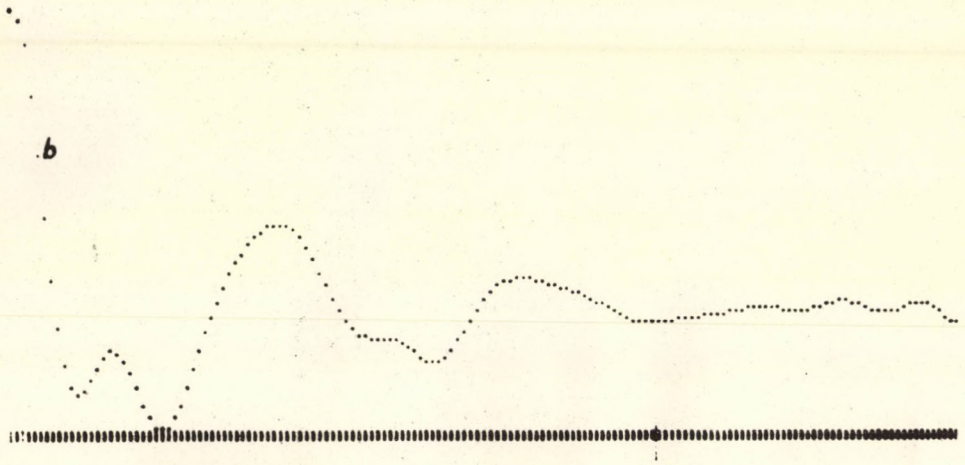


Fig. 5 Interferogram /upper curve/ and high resolution transformed spectrum/lower curve/ of uranyl-triscarbonate fluorescence spectrum

a/ Fourier Transform

In principle this method may be regarded as giving an exact solution to the problem, but a practical difficulty restricts its usage. This can be illustrated by Figures 6 and 7. In Fig. 6 the original spectrum of Fig. 5 has been superimposed with 1 per cent of noise /in normal distribution/ and in Fig. 7 with 5 per cent of noise. The Fourier transforms of the two spectra demonstrate well that the reliability of the information rapidly decreases with increasing noise /see Fig. 5/. With 1 per cent noise the

"limit of noise" can be easily evaluated but in the case of 5 per cent noise the information and the noise are not separable, so the method is unsuitable.



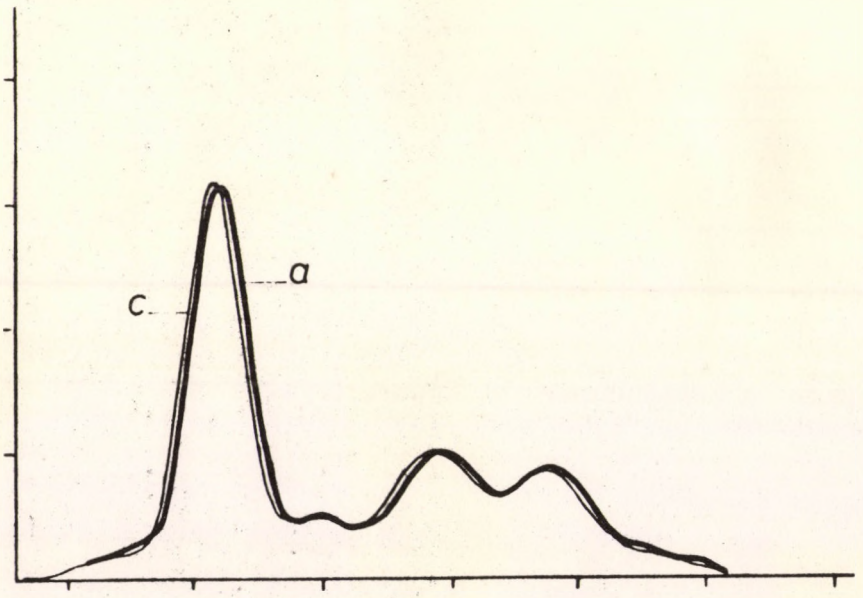
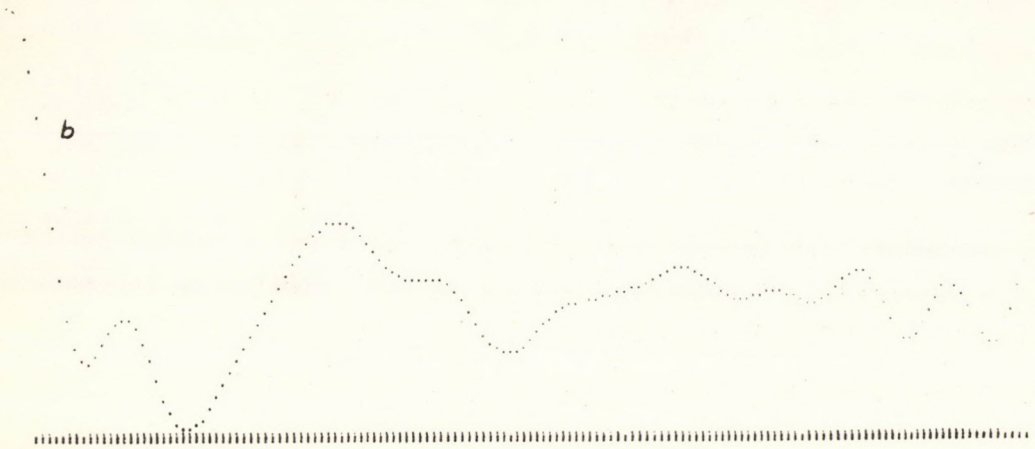


Fig. 6 Noise elimination by Fourier transform.

a: Noisy curve. Relative value of noise: ± 0.5 per cent.
b: Fourier transform of the noisy curve.
c: Retransformed spectrum.



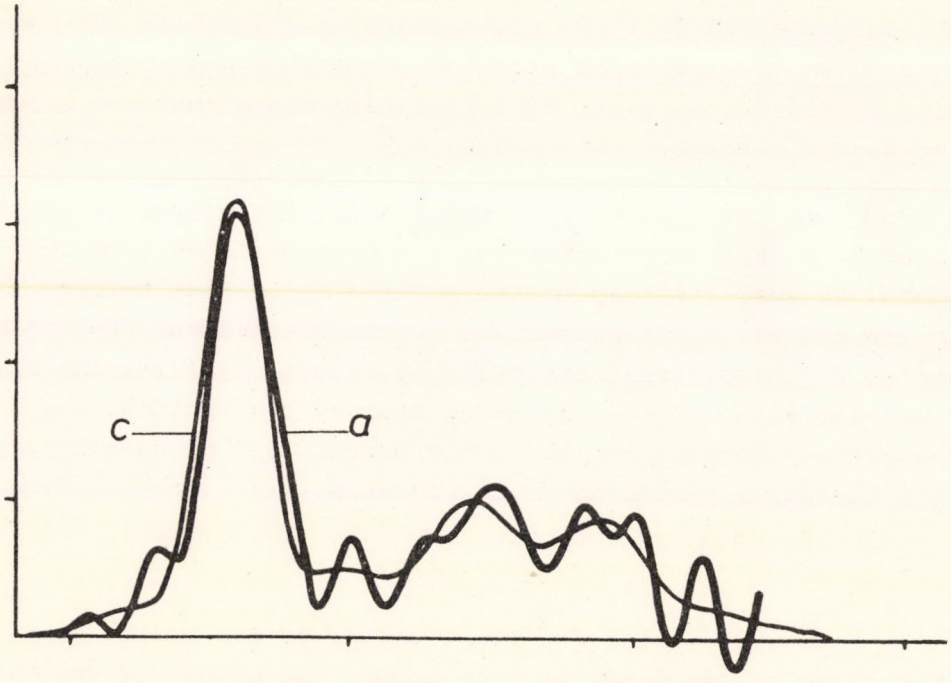


Fig. 7 Noise elimination by Fourier transform.

a: Noisy curve. Relative value of noise: ± 2.5 per cent.
b: Fourier transform of the noisy curve.
c: Retransformed curve.

b/ Convolutions

The most advanced procedure is based on the least square method developed by Savitzky and Golay [3]. This can be used successfully if the

experimental data are equidistant. The mathematical formalism is

$$Y_j^* = \sum_{i=-m}^{+m} \left(C_i \cdot Y_{j+i} / N \right)$$

where Y_j^* represents the data of the smoothed curve, C_i and I_j are the elements of the data points of the convolution function, and of original data array, respectively.

This procedure can be applied cyclically until the required extent of smoothing is obtained. The numerical values of the convolution function were given by Savitzky and Golay.

In our work convolution smoothing is also used in two other forms: five point quadratic and nine point quartic smoothing.

c/ Interpolation

A special application of the interpolation procedure for smoothing arises when the experimental data are not equidistant, which is the case usually encountered in spectroscopic practice. Smoothing has to be applied to the experimental points before their multiplication since the last procedure lends to the noise the character of information.

This procedure can also be used cyclically. The number of cycles can be determined by a logical condition or can be calculated from the experimental data. In the 5th step of the working cycle /see before/ the value of the noise and the cycle number /n/ of the measurement have to be determined. During the measurement the noise is reduced by $1/\sqrt{n}$. The remaining noise can be eliminated in the smoothing step by two factors: the length /k/ of the convolution function and the cycle number /N_c/ of smoothing. Both factors decrease the noise according to the formula

$$z/z_o = 1/(N_c.k)^{-2}$$

where z and z_o are the initial and final values of the noise, respectively. If the permitted value of the noise /z_j/ is known, the number of smoothing cycles can be calculated from the relation:

$$N_c = z_j^2/z_o^2 \cdot k$$

4/ Interpolation, multiplication and data selection

The smoothed data are usually not equidistant and the values of x-coordinates are not rounded off. In order to calculate the proper values of

a spectrum at correct coordinates, Lagrange's interpolation formula is used in the approximation to 5th degree. This method is applicable to multiplication of the experimental data as well, but in this case the spectrum must be noiseless.

Data selection is important for storage. It is preferable that the spectrum should contain the lowest number of points wich carry the complete information. The most effective factor to shorten a spectrum is to omit the x-coordinates, but this is possible only if the data array is equidistant. In this case the first x-coordinate and the interval between the coordinates must be known.

The interpolation formula is a very effective tool for data selection on the condition that the interpolation procedure can reproduce the original spectrum to the desired accuracy /less than 0.1 per cent/. The procedure reduces the data array by one-half in each cycle.

5/ Qualitative analysis of compounds

This type of work is extensively used in infrared spectroscopy. For these purpose the spectral data must be normalized. Here the most important parameters of the experimental spectra are the frequency and the intensity of peaks, the latter is usually given by a relative value /weak, medium, strong, etc./. For the determination of these parameters the first step in the evaluation is the so-called "peak-find" operation based on the Savitzky-Golay method [3]. The second step is a logical examination of the experimental data, using the conclusions from experimental spectroscopy.

This computer procedure is similar in structure to the conventional method but uses a huge mass of conclusions for the comparison and all statements are numerically evaluated.

6/ Fine structure of spectra

Mathematically defined, a spectrum consists of a number of components describing allowed and partly forbidden transitions. Their intensities vary in a wide range. Some bands overlap each other completely. The aim of spectroscopic work is to determine the parameters of the component band and to assign them to vibrations. However, the blurring of the fine structure as a result of the very complexity of the spectrum presents a considerable problem. The only workable analytical approach to the intense components of the spectrum is to take the low intensity components to be perturbations of the band shape. But this means that, if the Gaussian

distribution is accepted as the true shape of the component bands, the perturbation causes a Lorentzian-type distortion, and since the evaluation methods are not exact, this distortion can make the problem unsolvable. Nevertheless, in our experience the Gaussian approximation is effective if the perturbing bands are of low intensity. The analysis gives better results when a Voight approximation is used, where the band shape is described as a Gauss-Cauchy product function /see. in paragraph 6c./

$$F(\nu_i) = A_i \exp\left[-(\nu_o - \nu_i)^2/2\sigma^2\right] / \left[b^2-(\nu_o - \nu_i)^2\right]$$

In this case the mathematical procedure is more complicated because the approximation involves four parameters as compared with three of the Gaussian approximation. The time and memory required for the calculation increases exponentially with the number of parameters.

In our experience the spectrum components in electronic spectra can be adequately described by the Gaussian approximation. Using Voight approximation, the Gauss-Cauchy ratio can be 5:1 in a favourable case, but if the resolution of the fine structure is poor, it may be as small as 1:1. On the other hand, the experience in infrared spectroscopy is that the Cauchy approximation is usually dominant. [4]

After the general considerations we examine the steps of the spectrum analysis individually.

a/ Determination of the genuine spectrum

The genuine spectrum is free from instrumental distortions of whatever source /optical, electronic, mechanical/. The character of these effects can be described by the convolution

$$T(\nu_i) = \int_{-\infty}^{+\infty} K(\nu - \nu_i)\, S(\nu_i)\, d\nu \Big/ \int_{-\infty}^{+\infty} K(\nu) d\nu$$

Where $T(\nu_i)$ and $S(\nu_i)$ are the experimental and the genuine spectrum, respectively; and $K(\nu)$ is the instrument function /it simplifies the mathematical procedure if this is normalized to 1/.

Although the convolution broadens the bands of the spectrum and decreases its amplitude, it does not change the integral intensity. For practical spectroscopy the genuine spectrum is preferable because:

- it is completely independent of the instrument;

- the fine structure is more distinct than in the experimental spectrum;
- the determination of the energy value is more accurate
- the assignment is more reliable.

The elimination of instrumental distortions is a typical deconvolution problem

$$S(\nu_i) = \int_{-\infty}^{+\infty} \left[K(\nu - \nu_i)\right]^{-1} T(\nu_i)\, d\nu$$

In the solution of this equation the determination of the inverse function of $K(\nu)$ is problematic. The direct method is the Fourier transform, but the usefulness of this method is limited to cases where the noise is low. [5]

The indirect iterative computer method proves to be the best, since its application does not require complicated mathematical considerations and conditions. Details of the method are presented in a valuable summary by Seshadri and Jones. [4]

In our work the instrumental distortions are expressed by an experimental instrument function wich can be obtained from singlet spectral line. The finite slit effect is dominant in this function, wich is in the ideal case a triangle. As a result of optical aberrations this triangle becomes asymmetric and Gaussian in character. Fig. 7 shows an instrument function measured with a quartz spectrometer of Cary-Beckman type.

The deconvolution method we used was based on the Ψ -or pseudo-deconvolution technique developed by Jones et al. [6]

In order to improve the convergence multiplication by 2 was applied for correction in the first step.

In Fig. 9 the experimental /e/ and genuine /g/ spectrum of the fluorescence from uranyl-tris-carbonate are presented, where Fig. 8 has been used as an instrument function. The accuracy of the result is better than 0.1 per cent for all points /as can be tested by convolution/.

b/ Determination of the number of spectrum components

It was pointed out in the introduction to this section that there are various problems in the determination of the number and the apparent /suitable for calculation/ shape of component bands in a spectrum.

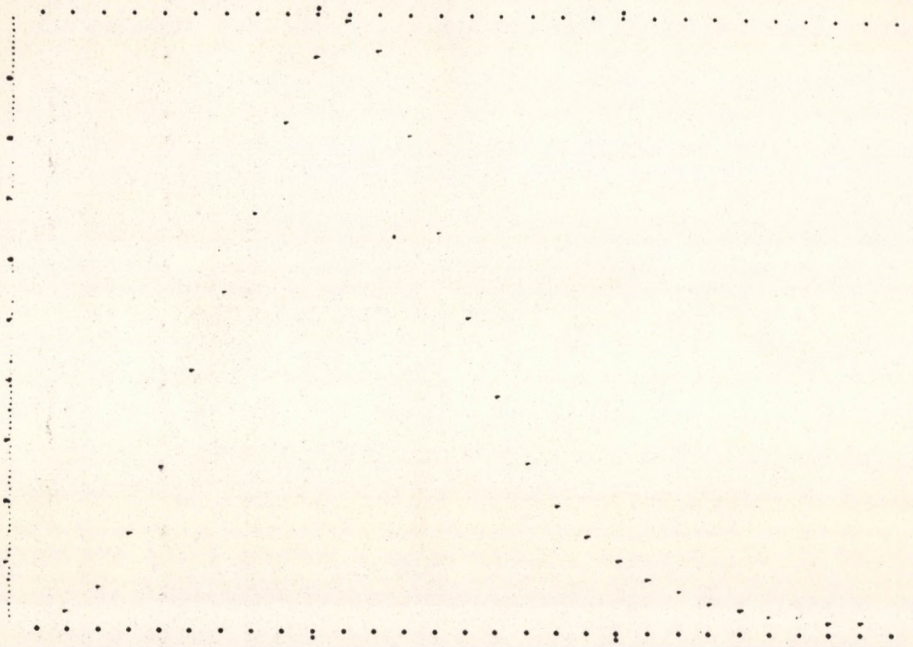


Fig. 8 Experimental instrument function

In a favourable case the number of component bands can be determined by simple inspection, but if this is not possible, it is necessary to use another method for the determination.

The derivative method is employed to determine the x-coordinates of the peaks and inflections. For this type of calculation the Savitzky-Golay method [3] was used. In our experience the derivative method does not give acceptable results if the fine structure is blurred or masked by noise.

The most elegant method is the Fourier transform, although this can only be used when the spectrum is free from noise. Assuming that the shapes of the component bands can be approximated by a Gaussian distribution function, it is valid for

$$f_k(\nu,\lambda) = A_k\left(\sigma_k^2/\left(\sigma_k^2 - \lambda\right)\right)^{-2} \exp\left[-\left(\nu-m_k\right)^2/\left(2\sigma_k^2-\lambda\right)\right]$$

If λ is suitable chosen, the different components are separated and thus the number of peaks /n/ can be counted and then the positions of the bands /m_k/ read off. The variance σ^2 can be evaluated from λ and the bandwidth

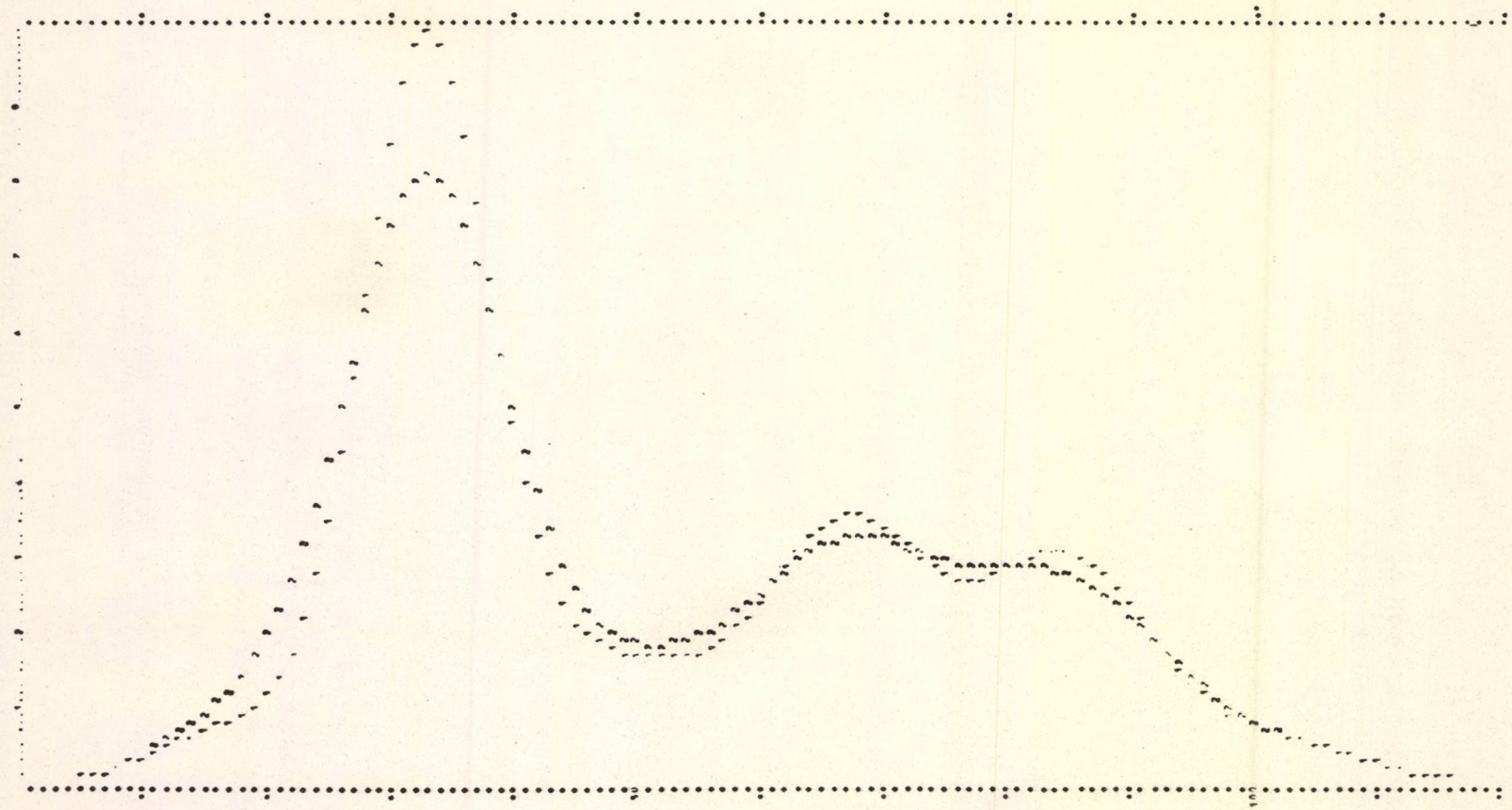


Fig. 9 Experimental /2/ and genuine /1/ spectrum of uranyl-tris-carbonate. The experimental instrument function is used for the deconvolution.

associated with the peak $/d_k/$ from the formula

$$\sigma^2 \approx d_k^2 + \lambda$$

while the amplitude A_k can be calculated from the intensity $/I_k/$ of the k-th peak and the bandwidth d as

$$A_k = I_k \, d_k \left(d_k^2 + \lambda\right)^{-1}$$

According to definition, the spectrum is

$$S(\nu) = \sum_k f_k(\nu, \lambda)$$

An example for that can be seen in Fig. 10 where the 0.0-bands of the fluorescence spectrum of uranyl-tris-carbonate are analysed. In this case the convolute function is almost as broad as the narrowest band in the spectrum.

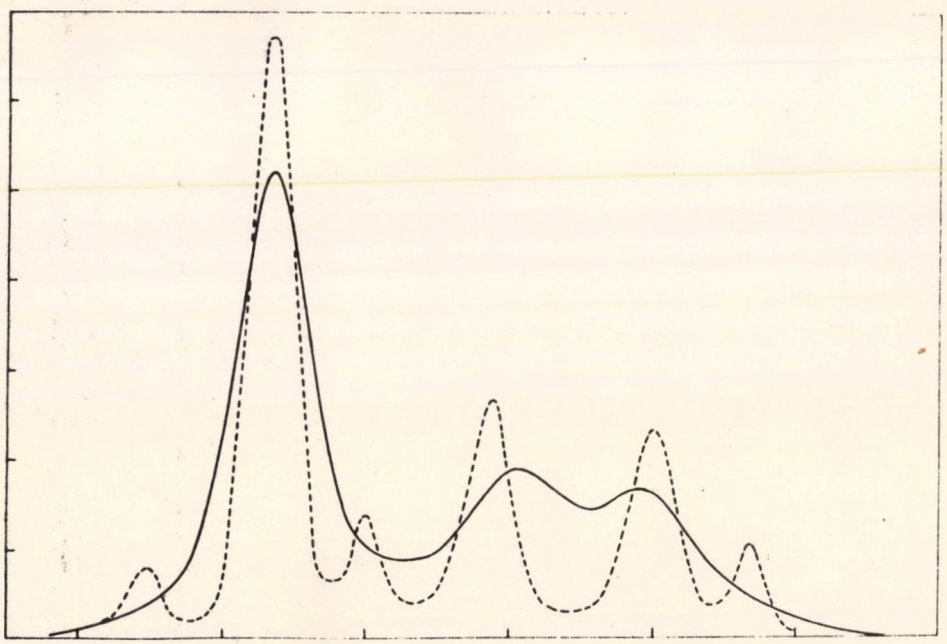


Fig. 10 Analysis of the component numbers of the 0.0-transition of uranyl-tris-carbonate fluorescence spectrum by Fourier transform.

An effective method proved to be the cyclically applied iterative deconvolution using a Gaussian band of narrow shape for the genuine spectrum. Fig. 11. shows the results of a calculation of this type. This method does

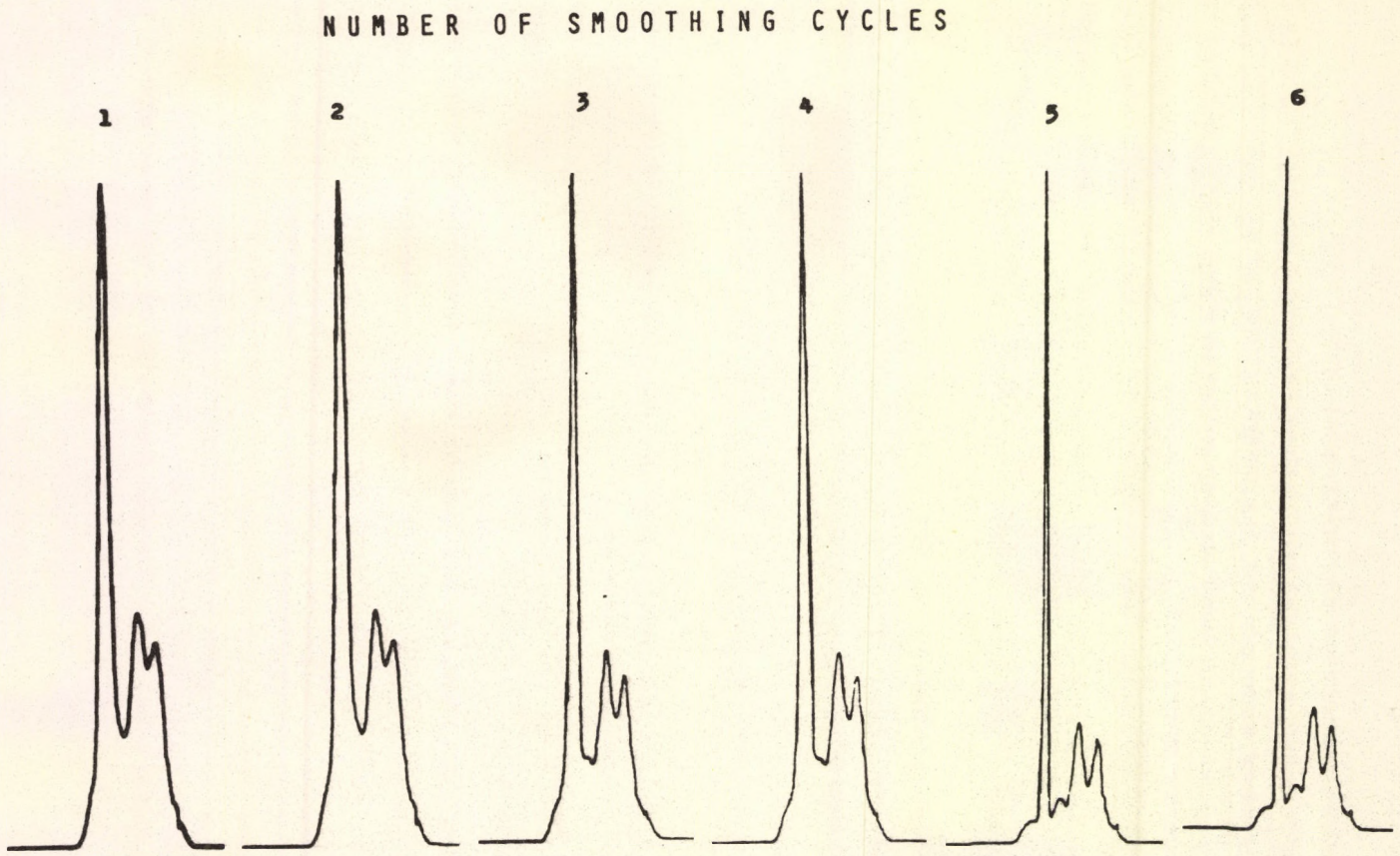


Fig. 11 Determination of the number of spectrum components by cyclical deconvolution.

not give better results than the Fourier transform, but it imposes fewer conditions of application .

An interesting method for determining the number of components is the so-called successive elimination method. In this case it is supposed that the low-frequency side of the spectrum is shaped by only one component. The parameters of a Gaussian band are calculated from the points of the low frequency side by the least squares method and the original spectrum is reduced by that component. The procedure is repeated until the residual spectrum is small enough. This method requires repeated visual control.

c/ Fitting procedure

This procedure serves to fit the experimental spectrum $S(\nu)$ with a calculated spectrum $f(\nu)$ defined by a parameter set to minimize the sum of square deviations

$$\sum_{i=1}^{N} W_i \left[S(\nu_i) - F(\nu_i, \bar{a}) \right]^2 = \text{minimum}$$

where W_i is the weighting factor due to the i-th point. Both spectra consist of N corresponding points.

The algorithm of the spectrum calculation is selected by the user. The only conditions are:

- the spectrum must be the sum of the positive component bands;
- the component bands can have only a single peak.

In our computation work the following types of component bands are used:

Gaussian components

$$f(\nu_i) = A \exp\left[-(\nu_o - \nu_i)^2 \left(2\sigma^2\right)^{-1} \right]$$

where A is the amplitude, ν_o is the position of the peak and σ^2 is the variance.

Cauchy components

$$f(\nu_i) = A \left[b^2 + (\nu_o - \nu_i)^2 \right]^{-1}$$

where 2b is the half-bandwidth.

Voigt components /Gauss-Cauchy product function/

$$f(\nu_i) = A.\exp\left[-(\nu_o - \nu_i)^2 \left(2\sigma^2\right)^{-1}\right]\left[b^2 + (\nu_o - \nu_i)^2\right]^{-1}$$

Sum of Gaussian and Cauchy functions

$$f(\nu_i) = A_G \exp\left[-(\nu_o - \nu_i)^2\left(2\sigma^2\right)^{-1}\right] + A_C\left[b^2 + (\nu_o - \nu_i)^2\right]^{-1}$$

where A_G and A_C are the amplitudes of the Gaussian and Cauchy components, respectively.

The Voigt and sum function gives information about the contributions of the Gauss and Cauchy functions to the experimental spectrum.

There are 3 parameters in the Gauss and Cauchy functions, 4 in the Voigt function and 5 in the Sum function /only the parameter ν_o is common to both functions/.

The calculated spectrum $F(\nu_i, \bar{a})$ is produced by summarizing the adequate points of the component bands:

$$F(\nu_i, \bar{a}) = \sum_{\ell=1}^{m} f_\ell\ \nu_i, \bar{a}$$

where $f(\nu_i, \bar{a})$ represents the values of the component bands at ν_i frequency and with a given parameter set. The forthcoming task is to find the minimum with respect to $\bar{a}$:

$$Q(\bar{a}) = \sum_{i=1}^{N} W_i\left[S(\nu_i) - F(\nu_i, \bar{a})\right]^2$$

The condition for the minimum is

$$-\frac{1}{2}\frac{\partial Q(\bar{a})}{\partial a_j} = \sum_{i=1}^{N} W_i\left[S(\nu_i) - F(\nu_i, \bar{a})\right]\frac{\partial F(\nu_i, \bar{a})}{\partial a_j} = q_j(\bar{a}) = 0$$

where $j = 1,2,\ldots,m$.

Then the transcendent equation system

$$\bar{q}(\bar{a}) = 0$$

is solved using the Newton-Raphson iteration method. If the k-th approximation

of the solution vector $\bar{a}$ is denoted by $\bar{a}^{(k)}$, the next approximation can be obtained by the iteration formula:

$$\bar{a}^{(k+1)} = \bar{a}^{(k)} + t^{(k)}\bar{p}$$

where

$$\bar{p} = -\left(\frac{d\bar{q}}{d\bar{a}}\right)^{-1} \bar{q}(\bar{a})$$

and $\left(\frac{d\bar{q}}{d\bar{a}}\right)^{-1}$ is the inverse of the derivative of the $\bar{q}$ vector-vector function with respect to $\bar{a}$.

In the case of more than 20 parameters it is convenient to analyse the spectrum in parts, and sometimes preferable to use Jones's moving subspace method. [7]

The system of normal equations becomes "ill conditioned" if the individual components are too near to one another and will thus cause convergence difficulties in the fitting procedure. Our program operates in the ill-conditioned case according to the steepest descent method [5]. This convergences in all cases although its rate of convergence may sometimes be exceedingly slow.

Fig. 12 demonstrate a least squares fit applied to the O.O - transitions of the fluorescence spectrum of uranyl-tris-carbonate. The spectrum was drawn by line printer.

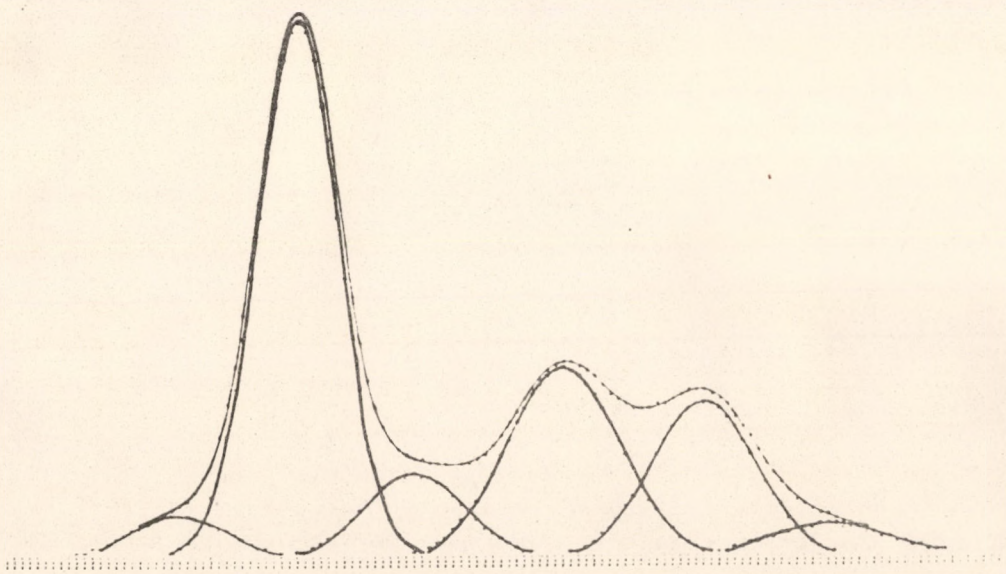


Fig. 12 Least square fit of the O.O-transition band of the uranyl-tris-carbonate ammonium salt fluorescence spectrum.

7/ Storage of spectra

During an experimental investigation a number of spectra are obtained. From the storage standpoint it is important to reject all unnecessary spectra containing redundant information. This category includes those spectra wich can be calculated from other spectra by a well defined mathematical process: spectra wich cannot be determined mathematically are called "core spectra". The core spectra are selected from the measurements and stored.

The core spectra are subjected to data selection for the reversible elimination of redundant data, as described in Chapter 4.

The organization of spectrum storage is not without its own problem, because there is no internationally accepted code system for chemical compounds. In our work we use simplified alphanumeric code system.

The standard spectra /see section 5/ are stored separately on magnetic tape. The blockhead of each standard spectrum contains the name of the compound and its most characteristic spectral parameters.

The core spectra are also stored on magnetic tape, but in this case the names of compounds form the basis of organization, and the blockhead gives information about the type of spectra stored.

8/ Usage of the spectrum library

The analytical standard spectra can be addressed sequentially in order of storing. The computer first compares the stored and analysed spectra with respect to their most important features /accumulated in the blockhead/. Once the most probable spectrum has been selected from the library, it is compared point to point with the normalized, investigated spectra. In many cases the data of the experimental spectra are not in agreement with the stored spectra and thus analysis fails. It has been found that logical methods of spectrum analysis by which the structural elements of the investigated compounds are estimated from the experimental spectrum using the computer version of the classical spectrum evaluation procedure /see section 5/ are more reliable.

The main adventage of having core-library is that it is capable of storing a very large number of spectra in a form easily accessible by computer. Detailed abstracts of the spectra stored for each compound, specifying the structural parameters, the number of spectra stored, the experimental conditions and the range of the calculable spectra can be made available by line printer for the investigator in printed form. The algorithms needed for the calculations are stored on magnetic tape and can be actuated by software.

At present only Lagrange's interpolation is used as an algorithm for calculation of the required spectra, multiplication of spectrum point, etc. The degree of the polynomial can be chosen freely. The spectra are mobilized in a suitable form by standard programming procedures.

SUMMARY

In the present report we summarized the experiences and results of the digital optical spectroscopic work performed in the Central Research Institute for Physics in Budapest. This work involves the development of the on-line spectrometers, the computerization of the spectrum evaluation work and the digital storing of the measured spectra.

In conclusion it can be stated that the digital methods of spectroscopy are suitable for the fast and precise evaluation of a multitude of data. The versatility of the instruments permits to obtain collect spectra under different conditions. It must be emphasized that the mathematical methods do not free the investigator from the detailed measuring work. They are valuable tools to obtain distinct and quantitative information from favourable experiments, and the experiments can be regarded as the primary source of information.

REFERENCES

[1] I.B. Berlman: Handbook of Fluorescence spectra of Aromatic Molecules Academic Press New-York, 1965.

[2] P.L. Richards: J. Opt. Soc. Am. 1964, 54, 1474.

[3] A. Savitzky and M.J.E. Golay: Anal. Chem. 1964, 36, 1627

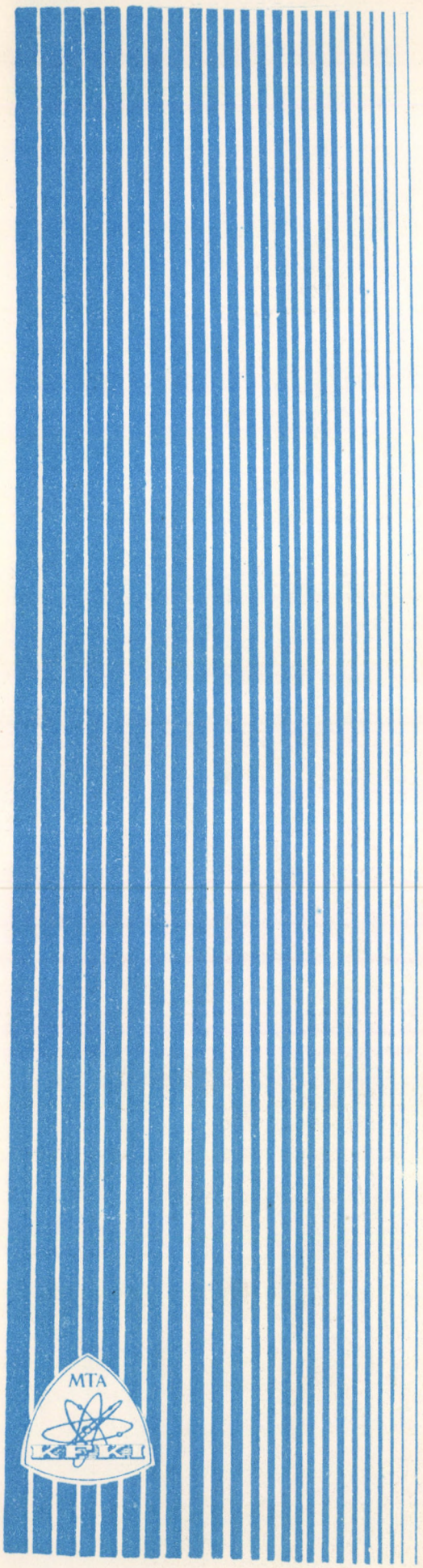
[4] K.S. Seshadri and R.N. Jones: Spectrochim. A. 1963, 19, 1013

[5] J Szőke, L. Varga and I. Nagypál: Proc. of Coll. Spectr. Interntl. XIV. Debrecen 1967, page 1905.

[6] R.N. Jones and R. Venkataraghavan: Spectrochim A. 1967. 23A, 925; 941.

[7] R.N. Jones and R.P. Young: Natl. Res. Counc. of Canada Bull. 13 page 37, 1969.

61.940



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Szabó Elek, a KFKI Kémiai Tudományos Tanácsának elnöke
Szakmai lektor: Kötél Gyula
Nyelvi lektor: T. Wilkinson
Példányszám: 310 Törzsszám: 72-6290
Készült a KFKI sokszorosító üzemében, Budapest, 1972. március hó